

1992-2017: 25 years of success story on Minor Actinides Partitioning Processes Development

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Abstract. In the frame of the successive 1991 and 2006 Waste Management Acts, French government supported a very significant R&D program on partitioning and transmutation of minor actinides (MA) in fast reactors. This program aimed to study potential solutions for still minimizing the quantity and the hazardousness of final waste, by MA recycling. Indeed, MA recycling can reduce the heat load and the radiotoxicity of most of the waste to be buried to a couple of hundred years, overcoming the concerns of the public related to the long-life of the waste. Over the 20 years of development, different types of strategies were studied, from the early multi-stage DIAMEX-SANEX processes to the most recent innovative SANEX, from the grouped extraction of MA thanks to the GANEX process to the most recent sole Americium recycling thanks to the EXAm process. These developments were supported by a robust and long-standing approach allowing successively to screen the potential extractants, to quantify their extractive properties and develop relevant chemical models to simulate it and to address their hydrolysis and radiolysis resistance. Finally, all these processes were qualified on a few kg of spent nuclear fuel within the Atalante CBP facility. This wide research program allows France to get a flexible portfolio of MA recycling processes that could be implemented after industrial upscaling. More recently, CEA initiated a demonstration experiment, the so-called integral experiment, which aims to re-irradiate in a Material Testing Reactor some fuel pellets manufactured from recycled UAm. Most recent results on these key experiments will be presented. Finally, several European Research Projects were funded in parallel by the European Commission and allow studying alternative separation processes. A general overview of these 20 years of successful and innovative research history will be synthesized in this presentation.

Key Words: Minor actinides, Transmutation, Fuel Cycle, Recycling

1. Introduction on the historical context

The French repository siting approach in the late 80's leads to a very controversial situation with important manifestation and opposition against the project. After a moratorium phase decided in 1990, the French Parliament voted in 1991 the first French Waste Management Act which gives 15 years to the French research to study 3 alternative routes for managing the ultimate waste: (i) evaluate the possibility of partitioning and transmuting the long-lived radionuclides (LLRN) to reduce the long-term toxicity of the waste, (ii) evaluate the feasibility of a deep-mined repository based on researches in Underground Research Labs, (iii) evaluate the possibility of upgrading the LLRN confinement and the possibility of a long-term interim storage. This so-called "Bataille's Law" was the starting point of a wide research program in France dealing with the potential partitioning of LLRN in view of their transmutation. Indeed, as reminded in Fig.1, spent nuclear fuel long-term toxicity is

dominated (i) first by plutonium which is already recycled in France thanks to the PUREX process, (ii) second by the minor actinides (MA: Am, Cm), then by long-lived fission products (LLFP). The rationale for this program was to evaluate the possibility of decreasing the waste radiotoxicity lifetime which is a major motivation for the population concern and opposition against a potential deep geological repository.

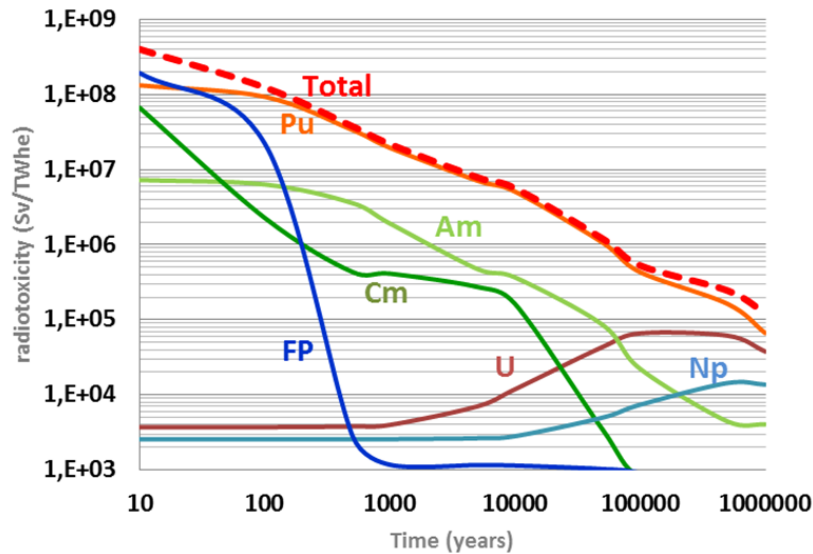


Fig.1: Evolution of the contribution of the different types of radionuclides to the long-term toxicity of spent nuclear fuels.

The program was dealing up to 2006 on the overall LLRN, both MA and LLFP, before being refocused around 2006 on the sole MA. The principle was to modify or complete the current industrial PUREX Pu-separation process to have access to LLRN. Several strategies were studied in parallel [1]:

- The so-called homogeneous recycling which is based on a dilution of MA in all the fuel assembly. It requires therefore a partitioning process able to recover MA together with Pu. Such a process is called Grouped Actinides Extraction, referred to as GANEX.
- The so-called heterogeneous recycling which is based on a concentration of the MA in dedicated blanket at the periphery of the reactor core to take benefit from the available neutrons in this zone without impacting the core neutronics. It requires therefore an enhanced partitioning process able to recover the MA in a dedicated flux. Such a process is called Enhanced Actinides Separation.

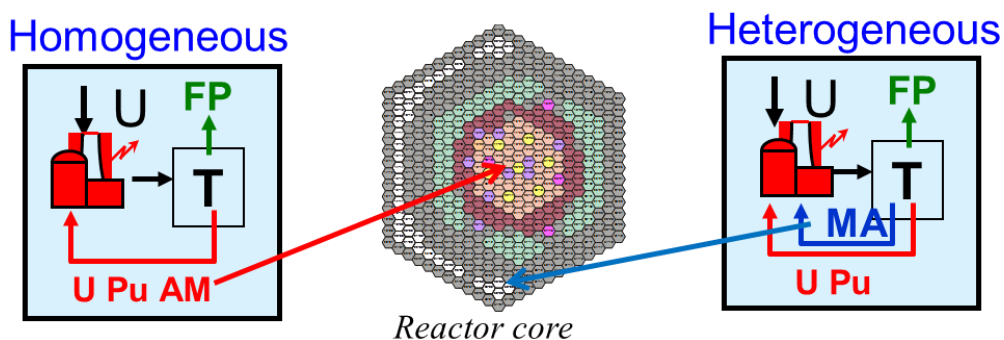


Fig.1: Description of the two options: homogeneous and heterogeneous recycling. T stands for the treatment plant, FP for Fission products, MA for Minor actinides.

This program gathered teams not only from the different CEA research centers, but also from Universities and CNRS and was extended to other European countries through several EU projects running in parallel to the French program and coordinated by CEA [2]. Furthermore, most of the key experiments on active materials, in particular the experiments on genuine spent nuclear fuel were conducted in the Atalante hotlab (CEA Marcoule, South-France) which started operating roughly at the same time in Dec.1992.

Around the term of this Law in 2006, CEA developed and tested several potential partitioning processes corresponding to the homogeneous and heterogeneous recycling. It also demonstrates that LLFP partitioning and transmutation (P&T) was not valuable for various reasons: (i) iodine is difficult to stabilise in a stable matrix in reactor conditions due to its volatility, (ii) caesium would require a prior isotopic separation step due to the high number of isotopes present in spent nuclear fuel, (iii) technetium transmutation is not efficient enough for being industrially deployed [3]. In this context, research on the LLFP partitioning will not be detailed in this paper.

In 2005, scientific external review as well as a public debate were organised to consolidate the main conclusions of these 15 years of research and prepare a new Waste and Nuclear Material Management Act which was voted on the 28th June 2006. Regarding P&T, this new law organised a new research phase of 6 years to allow the original P&T process for MA to be upgraded in order to demonstrate the industrial feasibility of MA P&T options. CEA issued in Mid-2012 a report to French government demonstrating that MA recycling may be implemented at a cost around ~5% of KWh [4]. Following this major milestone, CEA initiated an integral experiment aiming to demonstrate the possibility of recovering Am, fabricating new Am-bearing fuel and irradiating the fuel in a Material Testing Reactor. Following sections describes in more details these 25 years of history of the French research on nuclear materials recycling.

2. 1991-2005: the challenge of separating actinides and lanthanides

2.1. The chemical similarities of actinides and lanthanides

Minor actinides which are present at the stable +III oxidation degree in the spent fuel dissolution liquor at high nitric acid concentration, are not extracted by the classical PUREX neutral extractant TBP (tri-n-butyl phosphate). They are recovered as such in the PUREX raffinate. In order to separate them from this raffinate, it was necessary to design innovative processes using new extractant molecules. Several challenging stakes had to be overcome: (i) the high acidic of the medium ($C_{\text{HNO}_3} > 4\text{M}$) which induces a strong competition between H^+ and An^{3+} , (ii) the presence of a large panel of chemical elements (fission and corrosion products). Among them, the families to consider are the transition metals (Pd, Mo, Zr...) and the series of lanthanides which have very similar physico-chemical properties than Am and Cm, and are present at the same oxidation state +III [5].

For this reason, it is difficult to separate An(III) from Ln(III). These two series of elements are strongly hydrated and their ionic radii are close. Considered as hard acids in Pearson's Hard and Soft Acids and Bases theory, they react preferentially with hard bases, such as oxygen atoms bearing ligands (electron donors), via electrostatic interactions [6]. Their coordination numbers vary from 6 to 12 depending on the chemical system considered, and

their discrimination is therefore governed by size effects (fit of the geometry of the coordinating sites of the oxygen ligand with the radius of the metallic cation). However, a slight chemical behaviour difference does exist between the two series of trivalent elements: lanthanide $4f$ orbitals are slightly more localized around their nuclei than actinide $5f$ orbitals. Consequently, this property makes An(III) interact more easily with their electronic environments than the corresponding Ln(III) [7]. Unlike Ln(III), An(III) create stronger chemical bonds with “softer” donor atoms bearing ligands than oxygen, such as for instance sulphur or nitrogen [8]. The drawback of hydrophilic and/or lipophilic compounds containing sulphur and/or nitrogen atoms is their usually strong affinity for protons in acidic media.

In this context, developing a selective and efficient extracting molecule for separating minor actinides was a complex challenge and require an extensive R&D program allowing us to screen more than 100 molecules.

2.2 The basis of the DIAMEX/SANEX separation processes

Given the high acidity (3 to 4 mol.L⁻¹ HNO₃) and the composition of a PUREX raffinate (30 times more fission products including lanthanides (Ln) than minor actinides), the strategy adopted initially in the 90s was a selective stepwise extraction of actinides(III) (An(III)):

- First, the co-extraction of An(III) and Ln(III) by a malonamide, bidentate oxygen extractant (the so-called DIAMEX process),
- Second, the partitioning of the An(III) from the Ln(III) in a less acidic mixture using soft donor ligands (the so-called SANEX process),
- Third, the partitioning of Am from Cm with the SESAME process (oxidation and extraction of Am(VI) by tri-n-butyl phosphate) [9].

The key step of this process was the effective separation An(III) and Ln(III) thanks to the SANEX selective extraction of An(III). Many molecules bearing N atoms were produced and tested to increase the selectivity between An and Ln elements. The design of various molecules was widely studied in the frame of European collaborations (NEWPART, PARTNEW...). Many extracting systems were tested up to hot cell demonstration tests on genuine solutions [10-23].

In 2005, the feasibility of the minor actinide partitioning via the two steps DIAMEX-SANEX route was demonstrated on 15 kg of spent nuclear fuel: the coextraction of MA+Ln from other fission products thanks to the DIAMEX process, and the MA/Ln partitioning thanks to the SANEX process [25-25].

Finally, the final Am/Cm separation step, the SESAME process was designed to selectively recover oxidized Am to Am(VI). A hot test was performed but was not successful. The development of this separation process was stopped. A substitution process based on DIAMEX was then defined and successfully test for Am/Cm separation (DIAMEX2 process).

3. 2006 - 2012: Consolidating the previous processes and developing the sole-Americium separation processes, EXAm.

3.1 Consolidation of the GANEX processes

The GANEX process (Grouped ActiNide EXtraction) aims at the recovery of all transuranium elements from the HA spent fuel dissolution solution. It consists of two steps: selective extraction of uranium, and then partitioning of actinides from fission products and lanthanides.

The selective separation of uranium(VI) is operated by a hydrometallurgical process using a monoamide extractant DEHiBA (N,N-di-(ethyl-2-hexyl)isobutyramide) diluted in an industrial aliphatic solvent HTP. Based on batch experimental results, a physicochemical model was developed to describe the extraction of U, (Np), Pu, and Tc by DEHiBA. With the help of this model, a flowsheet was designed and tested in 28 mixer-settlers (laboratory scale) on a genuine High Liquid Waste (HLW) in the CBP hot cell (Atalante facility) in June 2008. After running 60 hours, more than 99.99% of the initial uranium was recovered with a good purity versus transuranium elements and fission products [26].

The GANEX 2nd step process consists of a group separation of transuranium elements (Np, Pu, Am, and Cm) by solvent extraction. The DIAMEX-SANEX process, initially developed for the partitioning of trivalent minor actinides (Am and Cm), was optimized to handle neptunium and plutonium along with americium and curium. Based on the experimental distribution ratios of actinides and major fission products, the initial DIAMEX-SANEX process was modified to allow the grouped actinide extraction GANEX by adjusting experimental conditions (selection of complexing agents, optimization of reagent concentrations) [27].

In terms of results, Np, Pu, Am and Cm were recovered altogether in a single flux (actinide product) and the losses of transuranium in the different outputs and in the solvent were estimated at a value lower than 0.5% (essentially neptunium) at the end of the test, corresponding to a recovery yield of actinides higher than 99.5%.

3.2 Consolidation of the DIAMEX/SANEX process

The scientific feasibility of the efficient Am and Cm recovery (yield > 99.9%) was demonstrated in 2005 through a 2-step process: (i) DIAMEX to coextract trivalent 4f and 5f elements (respectively Ln(III) and An(III)) and (ii) SANEX to selectively strip An(III) thanks to polyaminocarboxylate compound used in a buffered medium around pH = 3 (citrate buffer for example). Further improvements have been developed by CEA in order to get a simpler extraction scheme, in particular merging the DIAMEX and SANEX step, thanks to the use of another extracting molecules (TODGA) [28].

3.3 Development of the sole-Am separation process: EXAm

3.3.1. Motivations for recycling the sole americium

Although scientifically feasible, recycling Cm has been anticipated to be difficult to implement due to the very significant neutron emissions of Cm which would require very thick shielding at each step of the fuel cycle. In order to overcome this anticipated difficulty, a recent effort was focused on the recycling of sole-Am with the aim of assessing its viability. Indeed, it was demonstrated that recycling the sole-Am would allow us to save part of the gain of the full MA recycling while avoiding to handle the Cm in the fuel cycle. Furthermore, americium is also the main contributor to the residual heat power of the HLW waste after 100-120 years of decay as evidenced by Fig.4. In the French geological formation envisaged for hosting the deep geological repository, the heat power is a key factor for dimensioning the repository since the distance between HLW canisters needs to be high enough to limit the

temperature increase of the geological medium down to 90°C and prevent any transformation of the rock.

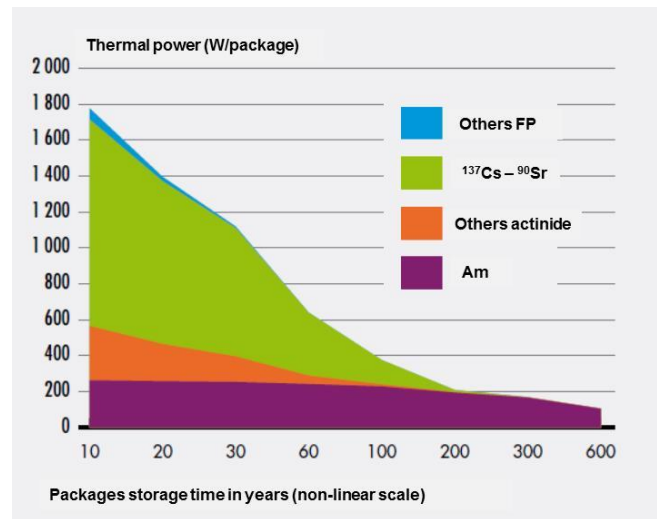


Fig.4: contribution of the various radionuclides to the long-term residual thermal power of HLW nuclear glass.

Based on these findings, new developments have been performed in France to develop and validate a partitioning process dedicated to the specific recycling of the sole Am (the so-called EXAm process).

3.3.2. Presentation of the EXAm process

The development of the EXAm process has taken benefit from the knowledge gained over the past twenty years on MA partitioning studies (supporting information). Under development since 2008, EXAm allows the separation of the americium alone from a PUREX raffinate in one cycle [29].

The first step is the americium extraction (Step 1). At this step, Am is separated from curium and heavy lanthanides. Light lanthanides, fission and corrosion products like Mo, Ru, Pd, Fe are also extracted in the organic phase together with Am. As some FP/corrosion products would be back-extracted with Am, it is necessary to add, a specific stripping step to remove these FP and corrosion products before the stripping of Am (Step 2). Then, Am is selectively separated from light lanthanides which remain in the organic phase like in the DIAMEX-SANEX/HDEHP process (Step 3). At the end, the light lanthanides are stripped from the organic phase to allow its recycling (Step 4). The general flowsheet of the EXAm process is given on Figure 5.

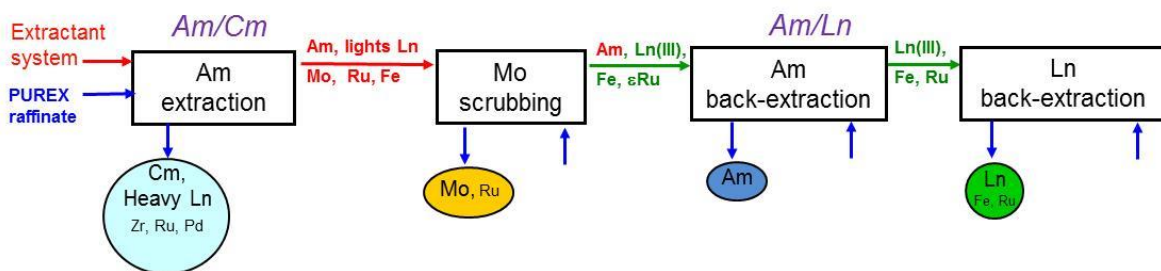


Fig.5: General flowsheet of the EXAm process

The EXAm process was successfully tested in Atalante on 5kg spent nuclear fuel in 2010. The hot test was carried out in the CBP cell using a set of 6 mixer-settlers batteries representing 68 separation stages (Fig. 6). A volume of 2.7 L of PUREX raffinate was successfully treated in a 54 h run and allowed recovering 98.3% of the initial Am. The purity of the recovered Am was good and the decontamination factor of Am versus Cm was greater than 500. The good control of the TEDGA concentration in the extraction and scrubbing stages is a key point of this process.

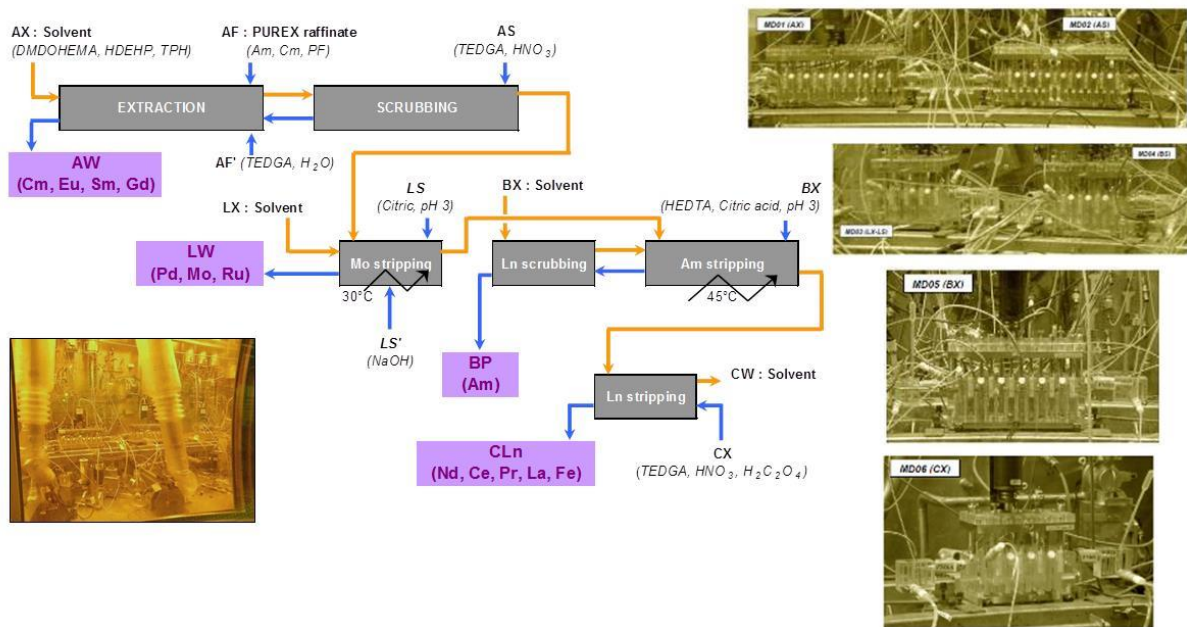


Fig.6: Experimental EXAm process flowsheet tested in CBP hot cell (Atalante facility) on genuine PUREX raffinate solution.

After this successful test, the process was improved by adapting it to concentrated solutions to ease its potential application at the industrial scale. The EXAm process for concentrated solutions was successfully tested in Atalante in 2015 on PUREX raffinates concentrated 3 times.

In parallel, alternative separation schemes were developed in the frame of the SACSESS project, in particular based on TPAEN. The separation of americium alone is achieved by co-extracting lanthanide (Ln(III)) and actinide (An(III)) cations into an organic phase containing the diglycolamide extractant TODGA, and then stripping Am(III) with selectivity towards Cm(III) and lanthanides with the water soluble ligand H₄TPAEN. Based on experimental data obtained by Jülich, NNL and CEA laboratories since 2013, a phenomenological model has been developed and implemented in the PAREX code. A flowsheet was proposed for a spiked test in centrifugal contactors performed with a simulated PUREX raffinate with trace amounts of Am and Cm. The chemical system appeared to be very sensitive to the concentration of nitrates and protons in the aqueous phase and still need to be improved [30].

4. 2012- 2020: The EXAm integral experiment.

Having a large set of potential MA recycling processes available, CEA decided to demonstrate the feasibility of implementing the Am recycling by launching an integral experiment, the aim of which was to recover Am from genuine spent nuclear fuel, to refabricate fuel pellet to be irradiated in a Material Testing Reactor. The experiment was launched in 2010 with the initial dissolution of 4.6 kg of spent nuclear fuels (mixture of 3 kg of UOX and 1.6 kg of MOX fuels) and the separation of U and Pu thanks to a COEX™ process. This allows recovering 2.5g of Am with a purity of 95.5 % due to the presence of remaining Cm (0.6%), lanthanides (1.7%) and Ru (1.1%). Conversion to powder is on-going in 2017 and should allow the pellets to be manufactured in 2018 in Atalante for an irradiated planned in 2020.

5. Conclusion

Minor actinides recycling for transmutation was identified in the early 90's as a potential route for improving the social acceptance of a future geological disposal of ultimate waste by decreasing the waste toxicity. For 25 years, France supported a very significant research effort in this direction which allows the development of a portfolio of 3 potential minor actinides recycling routes: (i) an homogeneous recycling of any minor actinides that could be therefore transmuted in fast neutron reactors fuels thanks to the GANEX process, (ii) an heterogeneous recycling of Am/Cm thanks to DIAMEX/SANEX partitioning process in minor-actinides bearing blanket fuel that could be implemented at the periphery of fast neutron reactors cores, (iii) finally the specific and sole recycling of americium thanks to the EXAm process, here also in blanket fuel. From the early time of screening and selecting extracting molecules in the mid-90's, the maturity of all these processes was very significantly increased and they have all been tested on actual commercial spent nuclear fuels in CBP in Atalante (CEA Marcoule). It allows us to progressively simplify the different processes as evidenced on the next figure.

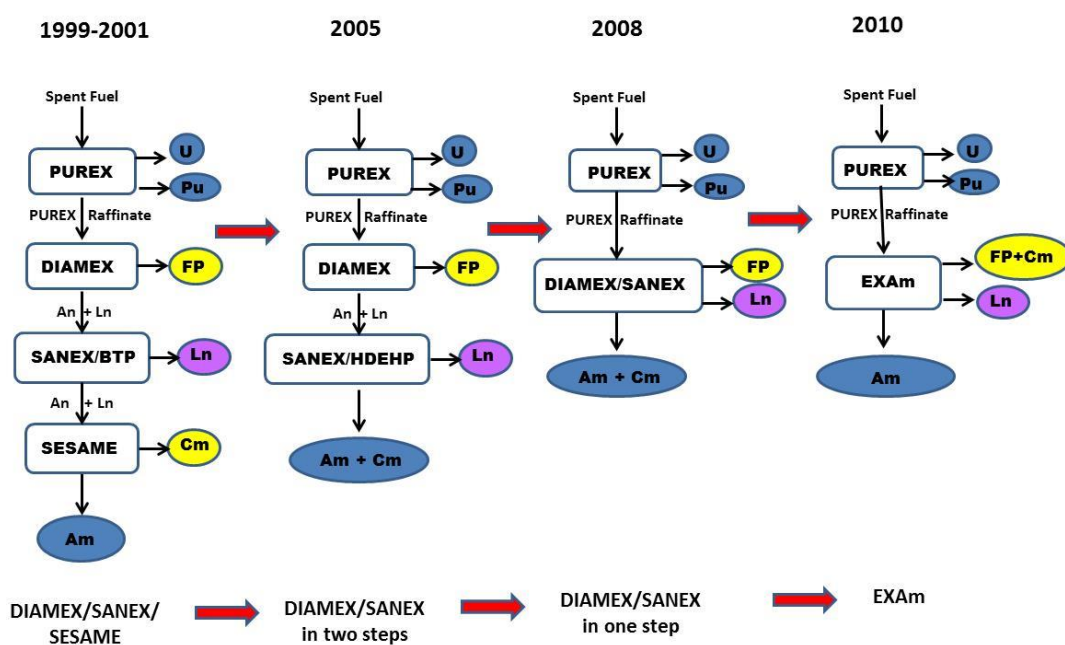


Fig.3: MA partitioning routes developed at the CEA

In order to achieve the demonstration of minor actinides recycling feasibility, an integral experiments is on-going and will allow us in a few years to introduce a few pellets manufactured with recycled americium within an experimental reactors. With this research program, France gets in hands all the requested information for taking in the future any potential decision for implementing minor actinides recycling. Research will be maintained in the future, although at a lower level, to optimize and simplify the current separation processes and therefore reduce the cost of such an option.

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